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(64) Production of para-diisopropylbenzene and use of the same in the production of hydroquinone.

(67) A process is disclosed whereby cumene is disproportionated in the presence of a ZSM-12 catalyst to selectively produce para-diisopropylbenzene. The para-diisopropylbenzene product may be oxidized to the corresponding dihydroperoxide followed by rearrangement to produce hydroquinone and acetone.

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PRODUCTION OF PARA-DIISOPROPYLBENZENE  
AND USE OF THE SAME IN THE PRODUCTION  
OF HYDROQUINONE

This invention relates to a process for the selective production of para-diisopropylbenzene by catalytic disproportionation of cumene and the conversion of the resultant para-diisopropylbenzene to hydroquinone.

Both para-diisopropylbenzene and hydroquinone have a number of commercial uses; para-diisopropylbenzene as a solvent and chemical intermediate and hydroquinone in photographic developers, medicines, dye intermediates, anti-oxidants, inhibitors, and stabilizers.

The disproportionation of aromatic hydrocarbons in the presence of zeolite catalysts has been described by Grandio et al. in the Oil and Gas Journal, Vol. 69, Number 48 (1971). In addition, U. S. Pat. Nos. 3,126,422; 3,413,374; 3,589,878; 3,589,879; and 3,607,961 show vapor phase disproportionation of toluene over various catalysts.

U. S. pat. No. 4,011,276 discloses disproportionation of toluene to produce benzene and xylenes rich in the para isomer with a catalyst comprising of crystalline aluminosilicate zeolite of the ZSM-5 type which ;has been modified by the addition thereto of a minor proportion of an oxide of magnesium. U.S. Patent No. 4,016,219 discloses a similar reaction but wherein the catalyst employed has been modified by the addition thereto of phosphorus in an amount of at least about 0.5 percent by weight. While the process of each of these patents show selective production of para-xylene, this is obtained only by tolerating a very substantial reduction in toluene conversion, i.e., decrease in activity compared to disproportionation of toluene carried out under comparable conditions with the unmodified zeolite catalyst.

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In these prior art processes, the xylene product produced either has the equilibrium composition of approximately 24 percent of para, 54 percent of meta and 22 percent of ortho or, in those instances where the para isomer is produced in an amount in excess of its equilibrium concentration, such is achieved only at great expense of activity, i.e., a very substantial reduction in toluene conversion. Of the xylene isomers, i.e., ortho-, meta- and para-xylene, meta xylene is the least desired product, with ortho- and para-xylene being the more desired products. Para-xylene, in substantial yield, is of particular value being useful in the manufacture of terephthalic acid which is an intermediate in the manufacture of synthetic fibers such as "Dacron". Mixtures of xylene isomers either alone or in further admixture with ethylbenzene have previously been separated by expensive superfractionation and multistage refrigeration steps. Such process, as will be realized, has involved high operation costs and has a limited yield.

In accordance with one aspect of the present invention, there is provided a process for the selective disproportionation of cumene with the selective production of para-diisopropylbenzene, said process comprising contacting said cumene with ZSM-12 catalyst under disproportionating conditions.

Suitable disproportionation conditions may include a temperature between 390°F. (200°C.) and 1,400°F. (760°C.) at a pressure between atmospheric and 1,000 psig (6,996 rPa) utilizing a feed weight hourly space velocity (WHSV) between 0.08 and 2.0. The latter WHSV is based upon the weight of catalyst composition, i.e., total weight of active catalyst and binder therefor. The effluent is separated and distilled to remove undesired products and to separate benzene, cumene and diisopropylbenzene. Unreacted cumene may be recycled.

In a further aspect, the invention resides in a process for the selective production of hydroquinone, said process comprising the steps of:

- (i) contacting cumene with a ZSM-12 catalyst under disproportionating conditions to selectively produce para-diisopropylbenzene and benzene;
- (ii) oxidizing said para-diisopropylbenzene of step (i) to the corresponding dihydroperoxide; and
- (iii) rearranging said dihydroperoxide product of step (ii) to produce hydroquinone and acetone.

The crystalline zeolite utilized herein is ZSM-12, the characteristics and synthesis of which are described in, for example, U. S. Patent No. 3,832,449, and EP-B-18089.

When prepared in the presence of organic cations, ZSM-12 is substantially catalytically inactive, possibly because the intracrystalline free space is occupied by organic cations from the forming solution. It may be activated by heating in an inert atmosphere at 540°C for one hour, for example, followed by base exchange with ammonium salts followed by calcination at 540°C in air. The presence of organic cations in the forming solution may not be absolutely essential to the formation of the zeolite. More generally, it is desirable to activate this type of catalyst by base exchange with ammonium salts followed by calcination in air at about 549°C for from about 15 minutes to about 24 hours.

When synthesized in the alkali metal form, the zeolite is conveniently converted to the hydrogen form, generally by intermediate formation of the ammonium form as a result of ammonium ion exchange and calcination of the ammonium form to yield the hydrogen form. In addition to the hydrogen form, other forms of the zeolite wherein the original alkali metal has been reduced to less than about 1.5 percent by weight may be used. Thus, the original alkali metal of the zeolite may be replaced by ion exchange with

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other suitable ions of Groups IB to VIII of the Periodic Table, including by way of example, nickel, copper, zinc, palladium, calcium or rare earth metals.

In practicing the present process, it may be desirable to incorporate the above described crystalline zeolite in another material resistant to the temperature and other conditions employed in the process. Such matrix materials include synthetic or naturally occurring substances as well as inorganic materials such as clay, silica and/or metal oxides. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Naturally occurring clays which can be composited with the zeolite include those of the montmorillonite and kaolin families, which families include the sub-bentonites and the kaolins commonly known as Dixie, McNamee-Georgia and Flordia clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite or anauxite. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification.

In addition to the foregoing materials, the zeolite employed herein may be composited with a porous matrix material, such as alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions, such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. The matrix may be in the form of a cogel. The relative proportions of zeolite component and inorganic oxide gel matrix on an anhydrous basis may vary widely with the zeolite content ranging from between 1 to 99 percent by weight and more usually in the range of 5 to 80 percent by weight of the dry composite.

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A second optional component of the ZSM-12 catalyst comprises a minor proportion, e.g., from 0.05% to 50% by weight of the catalyst composite, of a difficultly reducible oxide. Oxides of this type can include oxides of phosphorus as well as those oxides of the metals of Groups IA, IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, or VB of the Periodic Chart of the Elements (Fisher Scientific Company, Catalog No. 5-702-10) which serve to enhance the para-selectivity properties of the catalysts modified therewith. The difficultly reducible oxides most commonly employed to modify the selectivity properties of the catalyst are oxides of phosphorus and magnesium. Thus, the catalyst can be treated with phosphorus and/or magnesium compounds in the manner described in U.S. Patent Nos. 3,894,104; 4,049,573; 4,086,287; and 4,128,592.

Phosphorus, for example, can be incorporated into the catalyst at least in part in the form of phosphorus oxide in an amount of from 0.25% to 25% by weight of the catalyst composition, preferably from 0.7% to 15% by weight. Such incorporation can be readily effected by contacting the zeolite composite with a solution of an appropriate phosphorus compound, followed by drying and calcining to convert phosphorus in the zeolite to its oxide form. Preferred phosphorus-containing compounds include diphenyl phosphine chloride, trimethylphosphite and phosphorus trichloride, phosphoric acid, phenyl phosphine oxychloride, trimethylphosphate, diphenyl phosphinous acid, diphenyl phosphinic acid, diethylchlorothinophosphate, methyl acid phosphate and other alcohol- $P_2O_5$  reaction products. Particularly preferred are ammonium phosphates, including ammonium hydrogen phosphate,  $(NH_4)_2HPO_4$ , and ammonium dihydrogen phosphate,  $NH_4H_2PO_4$ . Calcination is generally conducted in the presence of oxygen at a temperature of at least about  $150^{\circ}C$ . However, higher temperatures, i.e., up to  $500^{\circ}C$  or higher are preferred. Such heating is generally carried out for 3-5 hours but may be extended to 24 hours or longer.

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Magnesium oxide is another preferred difficulty reducible oxide which can be incorporated with the zeolite composite in a manner similar to that employed with phosphorus. Magnesium can comprise from 0.25% to 25% by weight preferably from 1% to 15% by weight present at least in part as magnesium oxide. As with phosphorus, magnesium oxide incorporation is effected by contacting the zeolite composite with an appropriate magnesium compound followed by drying and calcining to convert magnesium in the zeolite to its oxide form. Preferred magnesium-containing compounds include magnesium nitrate and magnesium acetate. Calcination times and temperatures are generally the same as recited hereinbefore for calcination of the phosphorus-containing catalyst.

In addition to treatment of the zeolite to incorporate phosphorus and/or magnesium oxides, the zeolite may also be modified in a substantially similar manner to incorporate thereon a variety of other oxide materials to enhance para-selectivity. Such oxide materials include oxides of boron (U.S. 4,067,920); antimony (U.S. 3,979,472); beryllium (U.S. 4,260,843); Group VIIA Metals (U.S. 4,275,256); alkaline earth metals (U.S. 4,288,647); Group IB metals (U.S. 4,276,438); Group IVB metals (U.S. 4,278,827); Group VIA metals (U.S. 4,259,537); Group IA elements (U.S. 4,329,533); cadmium (U.S. 4,384,155); Group IIIB metals (U.S. 4,276,437); Group IVA metals (U.S. 4,302,620); Group VA metals (U.S. 4,302,621); and Group IIIA elements (U.S. 4,302,622).

By means of the present disproportionation reaction, it is possible to obtain a diisopropylbenzene product having, e.g., at least 60 percent of the para-isomer and, e.g., less than 1 percent of the ortho-isomer.

The process may be conducted with the cumene reactant in either the gaseous or the liquid phase. It may be carried out as a batch-type, semi-continuous or continuous operation utilizing a fixed, fluidized or moving bed catalyst system. The Example which follows will serve to illustrate the process of the invention.

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EXAMPLE

A steamed HZSM-12 catalyst having a silica to alumina ratio of 180, was tested for disproportionation of cumene. The hydrogen form of the zeolite was prepared by calcination,  $\text{NH}_4^+$ -ion exchange and final calcination. The zeolite was steamed for 3 hours at  $1000^\circ\text{F}$  ( $538^\circ\text{C}$ ), 100 percent steam and atmospheric pressure. The ZSM-12 was intimately mixed with 35 wt.% alumina binder, then pressed into wafers, crushed and screened to a uniform particle size of 14-20 mesh.

Reaction conditions and results are summarized in Table 1, wherein "CU" stands for cumene, "DIPB" stands for diisopropylbenzene and "NPRBZ" stands for n-propylbenzene.



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Table 1  
Cumene Disproportionation

Run No.	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Temp., °C	150	150	200	250
Pressure, psig (kPa)	500(3549)	500(3549)	500(3549)	500(3549)
CU WHSV	3.4	3.4	3.4	3.4
<u>Conversion, wt%</u>				
CU	3.2	2.6	13.2	45.1
<u>Selectivity, wt%</u>				
Benzene	33.3	39.7	33.6	34.2
DIPB				
para	14.7	14.1	26.9	21.5
meta	9.6	9.2	31.6	38.9
ortho	<u>0</u>	<u>0</u>	<u>.7</u>	<u>.5</u>
Total	24.3	23.3	59.2	60.9
NPRBZ	4.9	3.4	.7	.7
Other*	37.5	33.6	6.5	4.2
DIPB %				
para	60.5	60.6	45.5	35.3
meta	39.5	39.4	53.4	63.9
ortho	0	0	1.2	.8

\*Primarily propylene oligomers

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Conversion was relatively low at 150°C (3%) but increased to 13 and 45% at 200 and 250°C. Approximately equimolar amounts of benzene and DIPB were produced. At the latter higher temperatures, significantly more meta isomer (53-64%), compared with para (46-35%), was observed. The co-product benzene could be converted to cumene by alkylation with propylene for recycle. This could be a particularly practical extra step if a cumene plant were conveniently located.

The para-diisopropylbenzene product of the foregoing Example may be oxidized, e.g., with air, to the corresponding dihydroperoxide and rearranged by an acid catalyst to hydroquinone and acetone. The meta isomer is converted to resorcinol and acetone by an analogous process.

## WHAT IS CLAIMED IS:

1. A process for the selective disproportionation of cumene with the selective production of para-diisopropylbenzene, said process comprising contacting said cumene with ZSM-12 catalyst under disproportionating conditions.
2. A process for the selective production of hydroquinone, said process comprising the steps of:
  - (i) contacting cumene with a ZSM-12 catalyst under disproportionating conditions to selectively produce para-diisopropylbenzene and benzene;
  - (ii) oxidizing said para-diisopropylbenzene of step (i) to the corresponding dihydroperoxide; and
  - (iii) rearranging said dihydroperoxide product of step (ii) to produce hydroquinone and acetone.



European Patent  
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# EUROPEAN SEARCH REPORT

0149508

Application number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 85300013.1
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
Y	US - A - 4 367 359 (KAEDING) * Claims 1,4,11,12 * --	1	C 07 C 6/12 C 07 C 15/02 C 07 C 39/08
Y	GB - A - 764 338 (DISTILLERS COMPANY) * Claims 1,6,7; page 2, line 1 *	1	C 07 C 37/08 //C 01 B 33/28
A	US - A - 4 380 658 (CHU) * Claims 1,10,11 *	1	
A	US - A - 4 329 509 (HAAG et al.) * Claims 1,9 *	2	
A	US - A - 2 748 172 (RODGERS) * Column 6, lines 23-44 *	2	
D,A	US - A - 3 832 449 (ROSINSKI et al.) * Abstract * ----		
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 09-04-1985	Examiner KÖRBER
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document	